

**BONDING LIGNOCELLULOSIC MATERIALS**

The present invention relates to a method of forming products from lignocellulosic material in which the lignocellulosic material is subjected to a bonding operation using a phenol formaldehyde resin which is cured during said operation. The invention relates particularly (but not exclusively) to such methods in which lignocellulosic materials are bonded together, e.g. the production of phenolic resin bonded particle board and the production of plywood and other glued wood products.

The manufacture of particle boards involves the steps of forming a mixture of wood particles, a phenolic resin, and other additives and forming the mixture into what is known as a mattress. This mattress is then pressed into its final shape while heat is supplied to cure the resin. The time required to cure the resin so as to achieve satisfactory products is one of the factors determining the cost of the finished product as it governs the throughput that can be achieved. A satisfactory cure is needed to ensure that the final properties of the board are adequate for any particular end use. Such properties include water resistance (which is measured by examining the swelling of finished boards after soaking in water, and internal bond strength) since water can cause products made in this way to deteriorate resulting in a loss of bond strength with consequential swelling of the board and, in severe cases disintegration of the board. It is therefore desirable to improve the ability of such products to resist attack by water so as to obtain products with high dimensional stability.

GB-A-2 136 004 discloses the pre-treatment of wood particles with dibasic anhydrides to produce an esterified woody material which is used to form a moulding by mixing with an epoxy resin and effecting curing. The esterification reaction is carried out in the presence of a catalyst and, as exemplified, the reaction times vary from 7.5 minutes to 15 hours, the longest reaction times being used where the wood particles are chips of the kind used for producing particle boards. This prior specification includes a comparative example in which a particle board is made using a phenolic resin, but there is no suggestion of using the esterified wood in the manufacture of particle boards.

US-A-5 520 777 discloses a method of making fibreboard which includes forming a condensate of maleic anhydride and glycerol and impregnating wood chips with this condensate before the chips are transferred to a digester where, during steaming at an elevated pressure, an esterification reaction takes place between the components of the wood and the condensate. After digestion, the treated material is refined i.e. converted to fibre form under pressure. US-A-4 961 795 acknowledges at column 1, lines 35 to 45 that acids have been added to resole resins to accelerate the cure of phenol formaldehyde resins, and the prior art cited against this specification includes several specifications in which acids are added to phenol formaldehyde resins, either to control the rate of curing, or to increase the shelf life of resole resins whose initial formation involved manufacture at relatively high alkaline pH, as the higher the pH the shorter the shelf life of the resin. This means that if resins are e.g. manufactured at pH 11, the pH will be reduced to say 7 by the addition of e.g. sulphuric or oxalic acid before the resin is sold for use. US-A-4 001 186 describes such a process for stabilising a resin. US-A-4 961 795 describes the use of curing agents for phenol-formaldehyde which have an ester functional group selected from the group consisting of lactones, organic carbonates, carboxylic acid esters or mixtures thereof. These curing agents are added to the resin prior to its addition as a binder, and in order to avoid unacceptable increases in the viscosity of the resin so reducing the pot life of the resin as it becomes too viscous to handle a further additive in the form of an aliphatic alcohol is added to moderate the effect of the curing agent. There is no teaching in the specification concerning the pH at which curing takes place, but where possible to deduce this from the examples, it appears curing takes place at alkaline or neutral conditions.

According to the present invention there is provided a method of forming products from lignocellulosic material in which said material is subjected to a bonding operation using a phenol formaldehyde resin which is cured during said operation wherein at least one of maleic acid and maleic anhydride is added during the formation of such products so as to be in admixture with the resin when it is cured.

We have found that the inclusion of maleic anhydride and/or maleic acid in the phenol formaldehyde resin to be cured can be used either to achieve cost savings by reducing the quantity of resin required to achieve a product with adequate performance, or to enhance the performance that can be achieved with a particular quantity of resin and particular manufacturing conditions.

In the case where the resin is a solid (powder), the maleic anhydride and/or maleic acid may be incorporated in the resin to be cured by admixture with the resin prior to its application to the lignocellulosic material to be bonded. In the case where the resin is a liquid, the maleic anhydride and/or maleic acid may be incorporated into the liquid prior to application to lignocellulosic material. However, in this case, incorporation of the maleic acid and/or maleic anhydride into the liquid resin may affect the viscosity thereof and this may not be desirable, e.g. where it is desirable to spray the mixture of resin and maleic additive onto the lignocellulosic material. Alternatively, the maleic anhydride and/or maleic acid may be applied to the lignocellulosic material separately to application of the resole resin.

Therefore in contrast with the process disclosed in US-A-5 520 777, we have found that it is not necessary to go to the expense of converting the maleic anhydride into a condensate with glycerol. We can also avoid the need to impregnate the lignocellulose component since it is possible to merely apply the maleic anhydride or maleic acid either to the lignocellulose surface or admix it with the phenol formaldehyde resin. Additionally, the present invention avoids the extreme conditions required to esterify the lignocellulose.

If maleic acid is used as the additive for the phenol formaldehyde resin then it is possible that some or all of the maleic acid takes part in the curing process through conversion to the anhydride. The ability of maleic anhydride to become incorporated into the resin matrix is probably due to the electrophilic nature of the maleic anhydride molecule under the conditions used in forming a cured phenolic resin and the likelihood that it provides cross-links in the cured resin. We have found that other acidic anhydrides such as phthalic and succinic anhydride do not produce the

same benefit, possibly because they do not possess a suitable combination of acidic and electrophilic properties when curing a phenol formaldehyde resin. Strong acids, such as sulphuric acid, while capable of producing an improved product in terms of bond strength and water resistance, cannot be used because of the possibility of causing corrosion of the manufacturing plant, and in addition cause discoloration of the resin which can be seen in the finished product, which is unacceptable from a marketing point of view. Additionally, such strong acids can cause degradation of the board. Maleic acid and anhydride, though weaker acids, unexpectedly give a product equivalent in performance without the disadvantages arising from the use of strong acids.

Whilst the invention includes the use of mixtures of maleic anhydride and maleic acid there is however no advantage in using such a mixture as it simply means that two raw materials have to be utilised rather than choosing one. Moreover, for reasons of cost, maleic anhydride is preferred to maleic acid as the additive for use in the invention.

The phenol formaldehyde resin for use in the invention may be a novolac resin, in which case the maleic anhydride and/or maleic acid may substitute for at least a part of the curing agent (generally a compound capable of yielding formaldehyde) used for the cure of such resins. Furthermore, the maleic additive may substitute for at least part of the acidic curing agent normally used with such resins.

It is however more preferred that the phenol formaldehyde resin used in the method of the invention is a resole resin which may be an oligomer which is obtained by reaction of formaldehyde and phenol in the presence of an alkali, the oligomer being polymerisable when heated during pressing to form the cured resin which provides the bond.

It is preferred that the resole resin has a pH of at most 11.5, more preferably at most 11.0, and even more preferably at most 10.5. A particularly suitable pH is about 10.

An example of resole resin which may be used in the method of the invention is that sold by Neste Chemicals Ltd under the designation BD937.

The invention is applicable particularly in the bonding together of lignocellulosic material (e.g. in the manufacture of glued wood products, e.g. plywood) but may also be applied to the bonding of lignocellulosic materials to other substrates.

The invention finds particularly utility in the manufacture of particle board (for which the lignocellulosic material (e.g. wood or other plant residues) to be bonded together may be in the form of fibre, chips, shavings and/or flakes) and will be further described with reference to such products.

The invention therefore also includes in a process for manufacturing phenolic bonded wood particle board in which a mixture of lignocellulose particles and a phenolic resin are formed into a cured board under the action of heat and pressure, the improvement of providing in the mixture prior to pressing to form the cured board, at least one of maleic anhydride and maleic acid.

We have found that maleic anhydride and maleic acid can assist in obtaining a larger throughput of boards, because of a faster cure, and also gives an improvement in internal bond strength and water resistance over boards made under comparable conditions in the absence of the maleic anhydride acid additive. Moreover, by using maleic anhydride as the additive, the cost of the product may also be reduced since maleic anhydride costs less than the phenolic resin for which it may in part be substituted.

The quantity of maleic anhydride or maleic acid added is preferably in the range 5-55% by weight of the total weight of the resin and maleic anhydride and/or maleic acid, and more preferably 15-40% by weight on the same basis.

The combined amount of resin and maleic anhydride or acid used will vary according to the requirements of the product but usually ranges from 2% to 15% by weight of dry wood. Measurements are based in dry wood content but the wood chips used can contain as much as 14% by weight of water, and do not necessarily need to be dried before use. In this respect, we have found that maleic anhydride and maleic acid have the advantage of reducing sensitivity of the process (of producing particle board) to moisture and limit the effect of excess water on cure.

Maleic anhydride may be added as a solid or a liquid to the lignocellulose particles at the same time as the resin, or incorporated into the lignocellulose particle mix separately to the resin. It is also possible to spray molten maleic anhydride onto the lignocellulosic particles. Similar techniques may also be used in respect of maleic acid. The invention also includes dissolving maleic anhydride in water, thus forming a maleic acid solution and adding the maleic anhydride in this way to the system. It is possible that some or all of the maleic acid may react in the system in the anhydride form through decomposing back to the anhydride during the application of heat and pressure.

In forming phenolic resin lignocellulose particle boards, it is common to incorporate a wax emulsion into the mix. Maleic anhydride or maleic acid may be admixed into the wax emulsion prior to its addition to the lignocellulose particle mix.

A suitable wax was emulsion of a microstyalline wax is that sold under the trade name Mobilcer 538 by Mobil Ltd. We have found that a mixture of maleic acid and wax emulsion is made more stable by the further addition of a polybutene emulsion such as that sold by BP Chemicals under the trade name Hyvis polybutene.

Wax is sometimes added in the manufacture of particle board in a molten form, and in this case is usually sprayed onto the lignocellulose particles. In such a case, molten maleic anhydride may be sprayed on to the lignocellulose particles before, simultaneously with (but separately), admixed with, or after spraying with molten wax. Molten maleic anhydride may also be used in the absence of wax. It can

conveniently be sprayed onto e.g. lignocellulose chips during the final stage of a drying process. Similar techniques may also be employed with maleic acid.

A well known commercial form of particle board is oriented strand board (OSB). OSB is made from wood strands produced by slicing and milling wood. The strands will typically have dimensions of the order 50mm x 10mm x 2mm. The strands after drying are sprayed with hot wax and mixed with powdered phenolic resin. The strands are then formed into a mattress which is typically pressed at 200°C to cure the resin. The pressing time is measured in so many seconds per mm thickness of the mattress, and is typically chosen from the range 10-20 seconds per mm. The present invention could be applied to such a commercial process by adding maleic acid solution to the wood in the dryer, or spraying molten maleic anhydride along with the hot wax. The molten wax can also be replaced by a wax emulsion to which a solution of maleic acid has been added.

Although the invention has been described with particular reference to the production of particle board, it will be appreciated that the invention is applicable to other products obtained by bonding lignocellulosic materials. Examples of such products in which lignocellulosic materials are bonded together include plywood and other glued wood products. The invention is also applicable to the bonding of lignocellulosic materials to other substrates and may thus be applied, for example, to the production laminates from lignocellulose and resin impregnated paper, e.g. for the purpose of producing a decorative laminate.

The invention is further illustrated by the following non-limiting Examples and accompanying Figs 1 to 9 which illustrates the results of the Examples.

In all of the Examples the resole resin used was a commercially available resole resin sold by Neste Chemicals Ltd under the designation BD937. The boards were pressed at 200°C in a 150mm die to 12mm stops with a pre-heated punch. The test samples were conditioned according to the method BS5669 before being tested for internal bond strength and thickness swell after 24 hours soaking in water at 20°C,

and retained internal bond after drying at 60°C and re-conditioning according to the method of BS5669.

### Example 1

A series of boards was made using softwood chips with a moisture content of 4%, resin powder, various acids, and a mixture consisting of 80% by weight of Mobilcer 538 and 20% polybutene emulsion. The quantity wax mixture was 1.6% of the dry weight of wood. The various acids were mixed with the wax mixture before the wax/acid mixture was added to the wood. The quantity of maleic acid was used in the proportion of one part acid to three parts resin, dry weights. The other acids were added in sufficient quantity to maintain an equivalent molar ratio of acid to resin to that achieved by the maleic acid example. After mixing in the wax, sufficient resin was added to make the total dry weight of acid and dry weight of resin up to 5% of the dry weight of wood. Boards were obtained by pressing for three minutes.

The internal bonds and thickness swells of the boards were measured and the results are shown in Fig 1. The effect of the acids used on the colour of the cured resin were also observed with the following results:

Acidic material	pKa	resin colour
Sulphuric acid	-9	Black
p-toluene sulphonic acid	-6.5	Black
trichloroacetic acid	0.7	dark red
dichloroacetic acid	1.48	light yellow
maleic acid	1.83	light yellow

It can be seen from Fig 1, that (with the exception of maleic acid) the acids having a pKa value greater than 0 tended to give inferior internal bond strength and higher thickness swells than sulphuric acid and p-toluene sulphonic acid. However somewhat unexpectedly, maleic acid gave internal bond strengths and thickness



swelling values commensurate with those obtained using sulphuric acid and p-toluene sulphonic acid but had the advantage of providing a resin of light yellow colour as compared to the black cured resin obtained using sulphuric acid p-toluene sulphonic acid.

### Example 2

A series of boards were made to demonstrate the improved properties obtained by the addition of maleic acid. The wood was a soft wood shred with a moisture content of about 6 per cent. The wood shred was wetted with 2% by weight (based on the dry weight of wood) of Molibcer 538, then 5% by weight of resin (again, dry wood basis) was stirred in.

Boards were made with either no maleic acid or with 25% or 40% of the resin replaced by maleic acid. The maleic acid was added to the dried wood shred as a 30% aqueous solution (calculated as weight of anhydride to weight of solution) made by dissolving maleic anhydride in water. The acid solution was added before the wax dispersion. The boards were pressed for 2½, 3, 3½, 4, and 5 minutes.

Fig 2 shows the effect of replacing 40% of the resin with maleic acid on internal bond strength (IBS) obtained after pressing for the times and temperature specified. Fig 3 shows (again for 40% resin replacement) the IBS after soaking the series of boards in water for 24 hours at 20°C. Fig 4 shows the degree of thickness swell after the same treatment (for boards obtained by replacing 40% by resin).

Figs 5 to 7 are similar to Figs 2 to 4 but showing the result obtained with 25% resin replacement.

The results of these experiments clearly show the benefit of the addition of maleic acid achieving the development of satisfactory IBS, both initially and after soaking, as well as swell resistance. One way of expressing the improvements achieved is in the terms of the acceleration in the curing time in the reduction in time

required to achieve a particular strength, both initially and after soaking, to in the time to achieve a low level of thickness swell. It can be seen that with the addition of maleic acid both initial IBS development and IBS after cold soak is accelerated by about 4-6 sec/mm and swell resistance by about 5sec/mm.

### Example 3

Either powdered maleic anhydride or powdered maleic acid was mixed with powdered BD937 resin in the ratio of one part to three parts. 3g of Mobilcer 538 wax emulsion was stirred into 265g of wood chips with a moisture content of 10% for one minute. 12g of the mixture of resin and maleic anhydride was stirred in for a further minute. Control boards using 12g BD937 were made according to the same method. The boards were pressed for 3 minutes, 3½ minutes or 4 minutes. The boards made with maleic anhydride or maleic acid cured more quickly, had higher internal bond strength, swelled less in cold water, and had higher retained internal bond strength after soaking, as shown in Fig 8.

### Example 4

BD937 resin was made into a 50%, by weight, aqueous solution. 7.5% of the BD937 resin solution was mixed with wood chips, with a moisture content of 8.7%, for one minute and then 1.25%, by weight of dry wood, of maleic anhydride was mixed in for a further 1 minute. Control boards were made by mixing 10% of the BD937 resin solution, by weight of dry wood, with the wood chips. Boards were pressed for 3, 3½, 4, or 5 minutes. The boards made with maleic anhydride had higher internal bond strength, swelled less in cold water and had higher retained internal bond strength after soaking, as shown in Fig 9.

Examples 5 to 13 are provided to illustrate the various ways in which maleic acid and maleic anhydride may be added to improve the performance of resole resins. Boards were obtained by pressing for 2½ to 5 minutes and when tested gave results of the same order as this obtained in Examples 1 to 4.

### Example 5

Maleic anhydride was stirred into water to make a 30% w/w solution of maleic acid. Mobilcer 538 wax emulsion was mixed with Hyvis polybutene emulsion in the ratio 3:1. The maleic acid solution was mixed with the wax mixture in the ratio 10:3. 13g of the mixture was stirred into 250g of wood chips with a moisture content of 5.4% for 1 minute, followed by 9g powdered BD937 resin which was stirred in for 3 minutes.

### Example 6

Maleic anhydride was stirred into water to make a 30% w/w solution of maleic acid. 10g of this mixture and 3g of Mobilcer 538 wax emulsion were stirred into 250g of wood chips with a moisture content of 5.4% for 1 minute, followed by 9g powdered BD937 resin which was stirred in for 3 minutes.

### Example 7

Maleic anhydride was stirred into water to make a 30% w/w solution of maleic acid. 10g of this solution was sprayed onto 250g of wood chips with a moisture content of 11% while they were being stirred for 1 minute. 9g of powdered BD937 resin was stirred in for 1 minute.

### Example 8

BD937 resin was made into a solution of 50% solids content. 18g of this solution was stirred into 250g of wood chips with a moisture content of 11% for one minute. 3g of powdered maleic anhydride was then stirred in for 1 minute.

### Example 9

BD937 resin was made into a solution of 50% solids content. 18g of this solution and 3g of powdered maleic anhydride were stirred into 250g of wood chips with a moisture content of 11% for 2 minutes.

#### Example 10

BD937 resin was made into a solution of 50% solids content. 18g of this solution was stirred into 250g of woods chips with a moisture content of 11% for one minute. 3g of powdered maleic acid was then stirred in for one minute.

#### Example 11

BD937 resin was made into a solution of 50% solids content. 18g of this solution and 3g of powdered maleic acid were stirred into 250g of wood chips with a moisture content of 11% for 2 minutes.